## Carbon dioxide regulated nutrient demand in marine diatoms

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Marine phytoplankton fix carbon and grow in alkaline seawater with the aid of  $CO_2$  concentrating mechanisms (CCM), but an understanding of how the nutrient costs of phytoplankton CCMs are regulated by ambient CO2 is still emerging. This study examines the effects of  $CO_2$  on macronutrient demand in marine diatoms and its ecological and geochemical consequences. Nitrogen and phosphorus quotas in marine diatoms were inversely related to pCO<sub>2</sub> over the range of 150 ppm to 380 ppm CO<sub>2</sub>, but were relatively invariant from 380 ppm to 1500 ppm CO<sub>2</sub>. Carbon quotas showed small and inconsistent variation with pCO<sub>2</sub>, but the strong declines in N and P with increasing pCO<sub>2</sub> resulted in increasing C:N and C:P ratios with increasing pCO<sub>2</sub> resulted in increasing N:P ratios at higher pCO<sub>2</sub>.

The decline in diatom nutrient quotas as  $CO_2$  increases from 150 to 380 ppm will result in greater diatom biomass and a greater proportion of larger sized diatom cells. Lower diatom nutrient demands could have provided a negative feedback against past increases in atmospheric  $CO_2$  from glacial to postindustrial levels by supporting a higher diatom-driven oceanic carbon sink, but little nutrient relief of diatom growth is expected as  $CO_2$  levels rise above 380 ppm over the next 50 to 100 years since increasing diatom N:P ratios will drive surface oceans to more severe N limitation.

## Oxidation and transformation of nanoscale zero-valent iron in geochemically relevant waters

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Nanoscale zero-valent iron (NZVI) used for in situ groundwater remediation is highly reactive and oxidizes rapidly. To reduce aggregation, enhance mobility through the subsurface, and potentially target pollution zones polymer coatings are being applied to the NZVI surface. Although particles with engineered surface modifications are more mobile, they are up to 20 times less reactive than simmilar uncoated particles in ideal conditions. The reactivity and toxicity of NZVI in the subsurface depends on the extent of oxidation and the type of surface oxide or mineral phase that has formed on the particle surface. The interaction between NZVI and environmentally ubiquitous anions can potentially affect the extent of oxidation and the types of oxidation products that form.

NZVI particles, both bare and coated, were allowed to age in the presence of common groundwater anions, and excess dissolved oxygen, for various periods of time up to 6 months. X-ray absorption spectroscopy (XAS) was performed on the particles at Stanford Synchrotron Radiation Laboratory, beamline 10-2, at the Fe K-edge (7112). The resulting X-ray near edge structure (XANES) region of the spectra revealed the degree to which the anions had hindered NZVI oxidation. The extended X-ray absorption fine structure (EXAFS) region was fit using a library of Fe model compounds. A linear combination fitting technique, in conjunction with a principal component analysis, identified and quantified the mineral species that had formed. These results have implications regarding the reactivity, eventual fate, and potential toxicity of engineered iron nanoparticles.